

coordinates which satisfy the Eckart's conditions at non-stationary points of the PES [2]. Finally, the applicability of the Watson Hamiltonian for the description of non-linear molecules (near linearity) has always been questioned, since the Jacobian of the transformation that leads to the Watson Hamiltonian vanishes at the linear configuration. This results in singular behaviour of the Watson Hamiltonian, giving rise to serious numerical problems in the computation of vibrational spectra. In Ref. [3], we analysed the problem and proposed a simple solution. In solids [4], we studied the structural effects produced by the quantization of vibrational degrees of freedom in periodic crystals at zero temperature. To this end we introduced a methodology based on mapping a suitable subspace of the vibrational manifold and solving the Schrödinger equation in it. A number of increasingly accurate approximations ranging from the quasiharmonic approximation QHA to the vibrational self-consistent field VSCF method and the exact solution were studied. These methods were applied to study a linear H-F chain.

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S22 P737

Soft-mode behaviour of phonons in the CDW systems NbSe₂ and TiSe₂

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We investigated the soft-mode behaviour of phonons in the Charge Density Wave (CDW) systems NbSe₂ and TiSe₂, both theoretically in density functional theory (DFT) based on *ab initio* phonon calculations and experimentally by means of high resolution Inelastic X-ray Scattering (IXS). For both materials, the theoretical predictions for the phonon softening using the experimental lattice parameters coincide with the experimentally observed CDW instability behaviour: qualitatively for NbSe₂, quantitatively in TiSe₂. While TiSe₂ shows a rather sharp phonon anomaly at T=190K, the anomaly in NbSe₂ at T=33K is much broader than expected for a Fermi surface nesting driven CDW instability. Due to van der Waals bonding between the Se/Nb (Ti)/Se sandwiches the LDA and GGA approximations of the exchange-correlation potential lead to very different results for the equilibrium distance between these sandwiches. In all DFT calculations both NbSe₂ and TiSe₂ are described as metals where the Fermi surfaces are contributed by different electronic energy bands which may "dive" beneath the Fermi surface for a slight change of the geometry. For NbSe₂, we exclude Fermi surface nesting as main origin of the phonon softening. Contributions due to energy states more far apart from the Fermi surface seem to play a substantial role. For TiSe₂, there is no need to go beyond DFT in order to describe the phonon softening.

S22 P738

Momentum resolved electron-phonon interaction within the KKR formalism

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The momentum resolved Eliashberg function $\alpha^2F(\omega, k)$ was used to obtain corresponding momentum resolved self-energy Σ_k for the electron-phonon interaction. An expression for the calculation of the Eliashberg function $\alpha^2F(\omega, k)$ was obtained within the KKR Green's function formalism. All underlying calculations of the electron-phonon matrix elements as well as of the phonon energies are based on *ab initio* electronic structure calculations performed using the fully relativistic spin-polarized KKR band structure method. Applications have been done both for non-magnetic as well as for magnetic systems. Relativistic effects in the electron-phonon interaction have been analyzed. Theoretical results for Pb and Ni transition metals are compared with the experimental data.

S22 P739

First-principles study of lattice vibrations in perfect and defect kesterite-type Cu₂ZnSnSe₄ crystals

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We study, by applying the SIESTA method and the density functional theory, the electronic properties and lattice vibrations in kesterite-type Cu₂ZnSnSe₄ (CZTSe), a relatively novel important material for photovoltaic applications. From one side, the present analysis makes reference to earlier studies of structurally close chalcopyrite-type CuInSe₂ (CIS), one of so far most promising materials for thin film solar cells, whose applications are however hindered by relative rarity of indium. From the other side, a role of structural defects and non-stoichiometry in CZTSe makes an issue for the present study.

The interest for phonons is explained by high sensitivity of vibration frequencies to local elastic strains and to the presence of defects, which makes vibration spectroscopy a potentially important tool for the characterization of materials. However, the spectra of multinary materials are complicated and may profit from first-principles calculations for their unambiguous deciphering. We apply different ways to project phonon eigenvectors calculated in a supercell in order to identify genuine zone center modes, those corresponding to silent Raman modes in CIS, which may become observable in CZTSe due to reduced symmetry, and finally the defect-induced modes.

The phonon spectrum of kesterite is also interesting in the context of the percolation model for lattice vibrations in mixed semiconductors. Notably, the structure of kesterite is such that – looking at cation sublattices formed by Se anions – the Cu-sublattice is connected, whereas Sn and Zn are distant "impurities". The introduction of other impurities may have a twofold effect, due to a possible violation of the octet rule on doping and to variation of

the abovementioned connectivity. Such effects will be discussed, on the basis of density-functional calculations done for different supercells.

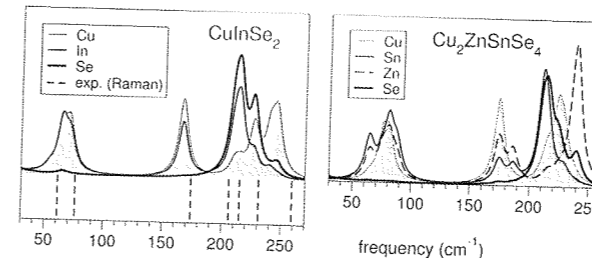


Figure 1: Zone-center vibration density of states (normalized per atom) in CIS and CSTSe.

S22 P740

Vibration modes in the "Ni₄" molecular magnet

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Ni₄, a shorthand notation for the [Mo₁₂O₃₀(μ₂-OH)₁₀H₂(Ni(H₂O)₃)₄·14 H₂O molecular magnet synthesized and characterized by Müller et al. [1] (note the usage of the Ni₄ notation for some different molecular magnets), contains four Ni ions at the edges of slightly distorted tetrahedron, connected by long (about 6.7Å) exchange paths Ni-O-Mo₂-O-Ni. The magnetization curve of this substance is unusual and impossible to explain within the standard Heisenberg model or its traditional extensions, without implying variations of exchange parameters with magnetic field and hence some magnetostrictive mechanism [2]. Extending previous studies [3] of electronic structure and magnetic interactions in the nominal experimentally determined structure and in the view of addressing elastic properties of the material, we now perform structure relaxation, followed by the evaluation of vibration modes, for its 104-atom molecular fragment. The (presumably small) coupling of molecules into a crystal is thus not taken into account, and consequently the vibration modes other than intramolecular ones are missing. The calculation is done by the Siesta method [4], using the generalized gradient approximation and phonons calculated by the finite-difference scheme. Moreover, molecular dynamics simulations have been done at different temperatures. The calculations reveal a broad spectrum of frequencies, starting with quite soft collective vibrations of the molecules (at about 100cm⁻¹) through Mo-O modes at 1000cm⁻¹ to high-frequency (~3700cm⁻¹) vibrations of water molecules. The modes involving the movement of Ni ions are numerous but effectively confined to a frequency range between 100 and 350cm⁻¹. Comparison with available experimental data and implications for magnetic properties will be discussed.

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S22 P741

Hole capture into oxide defects in MOS structures from first principles

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During the last decades, the evolution of semiconductor processing has led to constant shrinking of device sizes, with the smallest structures entering the regime of a few tens of nanometers in state-of-the-art technology. The benefits of this development – increased speed and functionality of integrated circuits – are accompanied by uprisng reliability issues caused by the amplified vulnerability of these tiny structures. One of the most important of these reliability issues is the negative bias temperature instability (NBTI) in p-doped metal oxide semiconductor field effect transistors (p-MOSFETs). It is encountered when a large negative voltage is applied to the gate contact, while all other terminals are grounded. The effect is amplified at elevated temperatures. Recently, a model for NBTI [1,2] has been developed at our group that is able to fit the observed degradation with unprecedented accuracy. It explains NBTI as a series of electrochemical reactions involving oxide defects and free charge carriers in the channel (see Image 1).

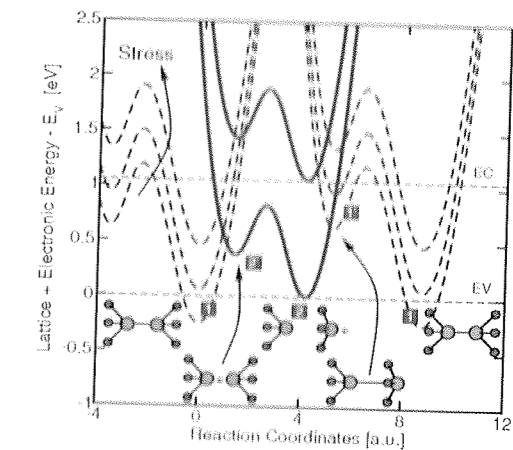


Figure 1: Schematic configuration coordinate diagram for the defect in our description of NBTI. As an example, the metastable configurations are illustrated for an oxygen vacancy. In the initial state (1), the defect is neutral and thus electrically invisible. Application of an electric field changes the relative position of the potential energy surfaces of the neutral and the charged defect. A detailed description can be found in [3].

It is the purpose of this work to study the atomistic foundation of our model and to ultimately find the defect responsible for NBTI. In this first effort, we concentrate on the initial charge transfer (transition 1 to 2') which is understood as a non radiative multiphonon hole capture process. The defects selected for inspection are the oxygen vacancy and the hydrogen bridge. The former has been previously suggested as the defect causing NBTI and other reliability issues, and the latter has been proposed as the defect causing stress-induced leakage current (SILC) [5].

Multiphonon capture: The transition of a hole from the semiconductor channel region to the defect is understood as a non radiative process involving multiple vibrational excitation of the defect structure. A detailed description

of the theory can be found in [3,4]. The central part of multiphonon theory is the line shape function.

$$f(E) = \text{avg}_{\eta_i, \eta_f} |\langle \eta_i | \eta_f \rangle|^2 \delta(E_f - E_i + E)$$

where η_i and η_f are the vibrational wavefunctions of the initial and final state and E_i and E_f are the respective energies. E is the energy of the tunneling hole.

The line-shape function dominates the hole energy dependence of the capture cross section $\sigma = \sigma_0 f$.

In this work, we apply the usual harmonic approximation to the dependence of the energy on the vibrational coordinates. Further we assume single mode coupling, treating the reaction coordinate of the hole capture transition as an eigenmode of the system. Using this approximation, the vibrational wavefunctions become simple harmonic oscillator wavefunctions. For the overlaps of the latter, analytic expressions are available in literature [6]. In contrast to previous studies which relied on empirical potentials matched to experimental data, the parameters of the parabolic potential are now taken from our *ab initio* calculations.

Calculation Method: The defects were placed in an orthorhombic alpha-quartz supercell. Alpha quartz was chosen because it is a well-studied reference for amorphous silica. The calculations have been performed using the Vienna *ab initio* simulation package (VASP) and the associated PAW pseudopotential database. The wavefunctions were expanded in a plane-wave basis set up to 800 eV, the total energy was calculated using the PBE functional. For the alignment of the defect energies with the silicon bulk, we follow the method of Blöchl [5]. Energies have been evaluated for the defects in their positive and neutral charge state for the positively charged and neutral optimum configuration. The results of these calculations are then used to parametrize the harmonic approximations to the adiabatic potential energy surfaces. Finally, life-time broadening is simulated by smearing the resulting dirac-peaks with a gaussian function of width $k_B T$.

Results: For the oxygen vacancy, a peak cross section approximately 1 eV above the SiO_2 valence band is predicted. From the crossing of the potential energy surfaces of the neutral and positive state, an activation energy of roughly 2.8 eV is predicted for the capture of holes from the silicon valence band, inconsistent with the assumptions in our NBTI model of about 0.6–1.2 eV.

A completely different behavior is found for the hydrogen bridge, which is predicted to be more stable in the positive state with a very small activation barrier for hole capture. The maximum of the capture cross section is found approximately 1 eV below the silicon valence level, indicating an efficient hole trap. The extracted parameters for the hydrogen bridge are in much better agreement with the parameters necessary to explain NBTI.

Further investigation is required using more sophisticated functionals and different alignment schemes to estimate the methodical error induced by DFT.

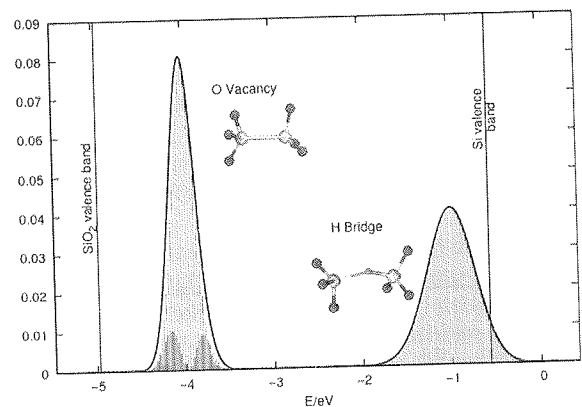


Figure 2: Calculated in-e-shape function at 300K for the oxygen vacancy and the hydrogen bridge.

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S22 P742

Analog of Rabi oscillations in resonant electron-ion systems

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Understanding quantum electron-ion correlations observed in organic semiconductors by ultrafast spectroscopy is the object of a renewed theoretical and computational effort. Since most of nonadiabatic molecular dynamics algorithms in use is not appropriate to simulate quantum electron-ion coherence in condensed phase, we have previously (J. Chem. Phys. 127, 214104 (2007)) introduced a better suited computational scheme based on Correlated Electron-Ion Dynamics (CEID). To illustrate its capability to simulate coherent quantum evolution of non-trivial atomic systems, we have studied a model displaying resonant oscillations analog of the Rabi oscillations considered in quantum optics. In particular, in our example we have found that quanta of vibration (phonons) play the role of the quanta of light (photons) and that the observed oscillations are due to quantum interference between different electron-phonon states. Finally, we discuss in details convergence and scaling properties of this improved CEID scheme and possible applications to semiempirical models of conjugated organic semiconductors.

Award

PS 1

PS 2

Authors